

# Chemical Synthesis of Lead Zirconate Titanate Nanowires

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## INTRODUCTION

One of the newest approaches to energy generation is energy scavenging. Energy scavenging seeks for ways to capture 'wasted' energy that is lost to the environment through everyday activities like walking. With every step, an average person weighing 68kg and walking at a pace of two steps per second loses about 67 Watts of energy to the environment<sup>1</sup>. While not all of that energy could be scavenged, a shoe insert might be able to retain a percentage of the wattage.

In order to scavenge this energy, specific nanomaterials are currently being investigated because they are small in scale and have desirable piezoelectric properties. A piezoelectric material will generate an electric potential difference and produce an electric field when mechanically stressed or strained. The reverse is also true, that when a material placed in an electric field, it will move or strain mechanically. This property is determined by the material's crystal structure, as all piezoelectric crystals are non-centrosymmetric, meaning that they do not have a center of symmetry. If the piezoelectric material can be coupled with a polymer and spun into a fiber, a collection of fibers can be used either in a shoe insert or in an a garment like a shirt to scavenge energy from human body movement.

The material we are interested in utilizing for energy scavenging is lead zirconate titanate (PZT). This material has been widely studied and is already being used in various applications such as IR detectors, microelectromechanical systems (MEMS)<sup>2</sup>, atomic force microscopy<sup>3,4</sup>, micromotors<sup>5</sup>. When no strain or electric field is applied to the PZT crystal structure exhibits a centrosymmetric perovskite cubic structure and the material has no net dipole. However, after poling occurs, where an electric field is applied across the material, the dipoles orientate themselves accordingly and the material has a net dipole. Poling and mechanical stress cause the PZT crystal structure to distort to a non-centrosymmetric tetragonal perovskite structure<sup>6</sup>. (See Figure 1)

Currently, while PZT is produced hydrothermally through different pathways, the majority of these methods require relatively high temperatures (>200°C) and increased pressure. The pressure increase is required in order to raise the boiling point of water above 100°C. The basic hydrothermal method is supplemented by other techniques, including electrophoretic growth, sometimes using a template<sup>7,8</sup>.

However, for the end application goal of this project, we need to produce PZT nanowires that are free from any additive like a surfactant, polymer, catalyst, or substrate. For ease of large-scale production in the future, it was also a goal to produce this material at low temperatures (100°C) and under atmospheric conditions.

## EXPERIMENTAL

To fabricate high aspect nanowires through a solution synthesis under atmospheric conditions, we chose to use a hydrothermal method. While this has been attempted in the past, the results have either been small nanoparticles<sup>3</sup>, branched nanobroomsticks<sup>4</sup>, and other powder morphologies not suited for our application<sup>5</sup>.

Xu *et al.* previously published a polymer-assisted method for hydrothermal synthesis of PZT<sup>9</sup>, however their reaction took place under high temperatures and pressure. We were able to adapt their method for use at 100°C and atmospheric pressure.

To synthesize the PZT nanowires, 0.1 M tetrabutyl titanate ( $[\text{C}_4\text{H}_9\text{O}]_4\text{Ti}$ ) solution in ethanol and 0.08M zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) were co-precipitated in a 0.15M  $\text{NH}_3$  solution with stirring. The resulting precipitate (ZTOH) was washed and filtered with water before being added to a round bottom flask. Enough water was added to make a 0.1M ZTOH solution. To this was added lead nitrate (0.11M), potassium hydroxide (2M), poly(vinyl) acid (PVA) ( $0.4\text{g/L}$ ), and poly(acrylic) acid ( $5\text{g/L}$ ). A general reflux setup was used (see Figure 2), heating was accomplished through an electric mantle, and the reaction ran for 24hrs.

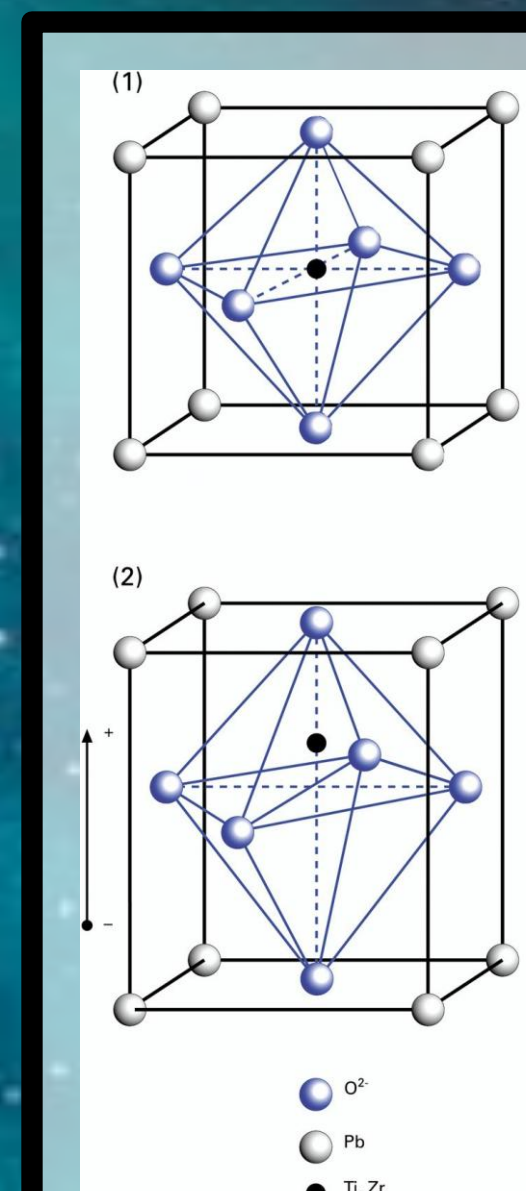


Figure 1: Graphic showing the change in centrosymmetry (1) before and (2) after poling or mechanical strain. This change causes the material to be piezoelectric.

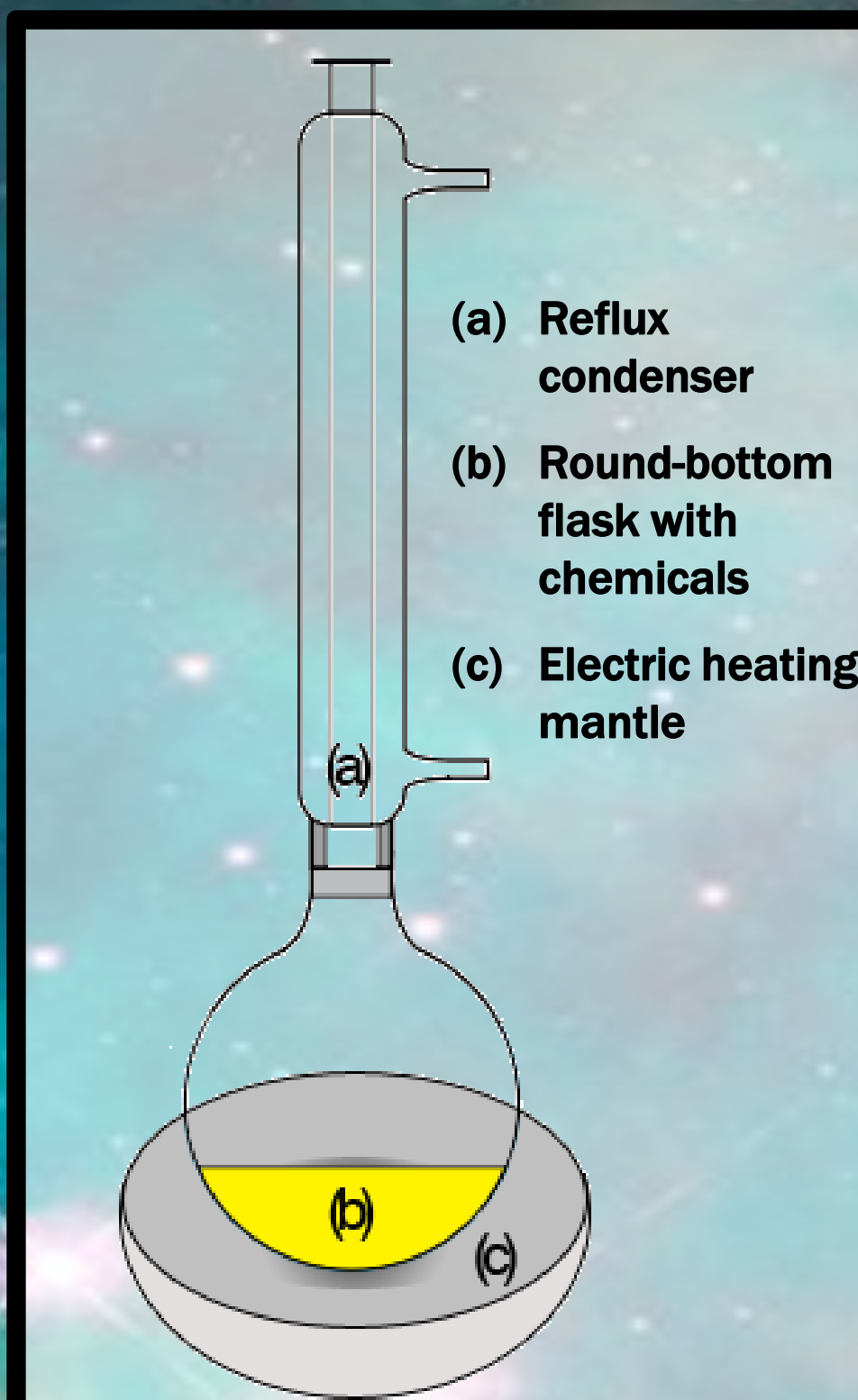


Figure 2: General reflux set up used in the hydrothermal synthesis of PZT nanowires.

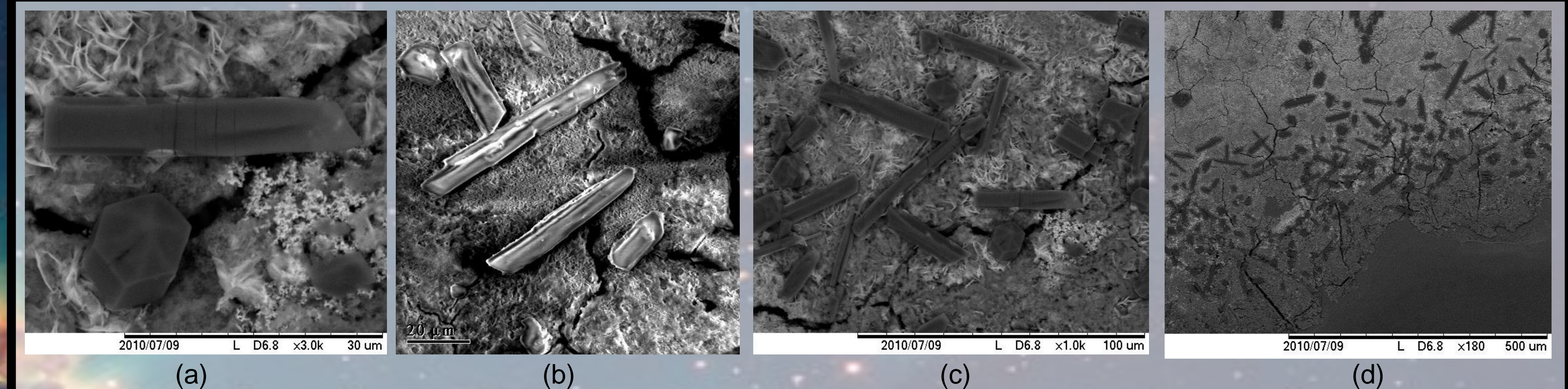


Figure 3: (a)-(d) SEM images of PZT nanowires embedded in other reaction products.

## RESULTS and DISCUSSION

Early results indicate that we are able to synthesize the nanoscale PZT using our experimental method. The nanowires appear to have six sides and are wider than our ideal. For ease of electrospinning the nanowires, the nanowires need to have a high aspect ratio. Xu *et al.* suggest that the PVA/PAA ratio aids in limiting the width-wise growth of the nanowires because the polymers have a higher affinity for the side surfaces over the top face, adhering more to the sides and halting growth outwards<sup>9</sup>. Due to the small scale of our reaction and light weight of the reactants, there is a possibility that the full amount of PVA is not getting in to the reaction beaker and thus affecting the width of our nanowires. More insight on this point and other factors affecting the reaction will be gained with further testing.

Separating the PZT nanowires from the rest of the products is one challenge we discovered while experimenting, as the nanowires are small in scale and either remain caught up in the polymer product or fall through the filter paper. According to the paper by Xu *et al.*, the nanowires may still have a polymer coating on all four sides even when they have been separated from the clumpy polymer product, however we have not yet been able to confirm this. Should this be the case in our reaction, we will also need to develop a method to dissolve the PVA and PAA from the PZT nanowires before they are used for our application for energy scavenging.

Once we can effectively clean and separate the PZT from the rest of the products, we will continue to characterize the nanowires by SEM, Raman spectroscopy, energy dispersive X-ray spectroscopy, and potentially build a device to test the piezoelectricity using atomic force microscopy.

## SUMMARY and FUTURE WORK

In summary, we have produced PZT nanowires through a hydrothermal synthesis at 100°C and normal atmospheric pressure. In the future, we would like to increase the reproducibility of the experiment and scale up the reaction. We would also like to increase the aspect ratio by decreasing the width of the nanowires and we would like to decrease the dependence of the reaction on the addition of polymers.

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